

APPLICATION FOR UNITED STATES LETTERS PATENT

TITLE:	Flexible Tubing
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## TECHNICAL FIELD

This invention relates flexible tubing for use in aqueous systems and more particularly for use in systems for collecting and distributing milk. More specifically, 5 this invention relates to flexible elastomeric tubing having an inner wall made of bacteria resistant thermoplastic silicone rubber and an outer wall of polymeric rubber derived from polymer blends comprising olefinic polymers.

## BACKGROUND ART

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Construction of automatic milking apparatus has been recognized as an important consideration in the dairy industry. Bacterial contamination of the milking machines or systems contributes to mastitis, and therefore efforts have been made in hygienic construction of the milking apparatus.

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Potential habitats for bacteria include such areas as the inside of milk tubes, rubber gaskets and cracks in the various parts of milking systems. This also includes microhabitats created by microscopic surface cracks which exist in the rubber tubing. The surface cracks of conventional rubber parts e.g. tubing becomes more severe with usage. For purposes of this invention, the use of thermoplastic silicone rubber (TSR) for 20 milk hose lines or tubing is required, inasmuch as silicone rubber tubing does not exhibit surface cracks or bacteria contamination as experienced with conventional rubber, and the habitats for bacterial propagation is greatly minimized. Therefore, the use of

thermoplastic silicone rubber tubes is expected to minimize the bacteria contamination in conventional rubber tubing used in the milk industry.

### DISCLOSURE OF INVENTION

5           This invention relates to flexible elastomeric tubing comprising laminated polymeric materials wherein the tubing has an inner wall substantially resistant to bacteria growth consisting essentially of a thermoplastic silicone rubber with the outer wall comprising polymeric rubber derived from a polymer blend comprising olefin polymers. The polymeric rubber of the outer wall is derived from a polymeric blend  
10   comprising from about 10 to 30 parts by weight of an olefinic copolymer, 25 to 50 parts by weight of an olefin-styrene block copolymer, 25 to 50 parts by weight of a thermoplastic rubber, or as an alternative an ethylene-vinyl acetate copolymer, 2 to 15 parts by weight of a maleic anhydride-olefin copolymer and 0 to 1.0 part by weight of a phenolic resin. The flexible tubing of this invention is particularly useful for conveying  
15   aqueous liquids such as milk or water because of the resistance of the thermoplastic silicone rubber (TSR) to bacteria growth.

          It is therefore an object of this invention to provide flexible tubing for conveying aqueous liquids wherein the inner wall of the tubing comprises a thermoplastic silicone rubber.

20           It is another object of this invention to provide flexible tubing of multi-layer construction wherein the inner layer of the tubing comprises a thermoplastic silicone rubber.

It is a further object of this invention to provide a process of conveying an aqueous liquid through flexible tubing substantially resistant to bacteria.

It is still a further object of this invention to provide flexible tubing for aqueous systems wherein the inner wall of said tubing comprises thermoplastic silicone rubber which is substantially bacteria resistant and provides sanitary conditions with the outer wall of said tubing comprising polymeric rubber derived from a polymer blend comprising olefin polymers.

These and other objects of this invention will become apparent from a further and more detailed description of the invention.

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#### BEST MODES FOR CARRYING OUT INVENTION

This invention relates to flexible elastomeric tubing and more specifically to tubing particularly useful in aqueous systems including the elastomeric tubing used in milking machines. The elastomeric tubing is derived from laminated polymeric materials wherein the inner wall of the tubing is substantially resistant to bacteria and consist essentially of thermoplastic silicone rubber (TSR) with the outer wall comprising a particular polymeric rubber. The polymeric rubber of the outer wall of the tubing is derived from a polymeric blend of polymers and copolymers comprising from about 10 to 30 parts by weight and preferably 15 to 25 parts by weight of an olefinic copolymer derived from lower molecular weight olefins, 25 to 50 parts by weight and preferably 35 to 40 parts by weight of a styrene-olefin block copolymer, 25 to 50 parts by weight and preferably 35 to 40 parts by weight of a particular thermoplastic rubber or as an

alternative an ethylene-vinyl acetate copolymer (EVA), 2 to 15 parts by weight and preferably 4.0 to 10 parts by weight of maleic anhydride-olefinic copolymer, and 0 to 1.0 parts by weight and preferably 0.4 to 0.6 parts by weight of a phenolic resin.

5 The thermoplastic silicone rubber of the inner wall of the tubing is available from the Dow Corning Co. as TPSiV, and is characterized as a vulcanized silicone thermoplastic resin that can be extruded on conventional thermoplastic processing equipment in preparing laminates from which the tubing is prepared.

TPSiV materials can be extruded on conventional processing equipment. The screw L/D should be at least 24:1 with a compression ratio of 2.5:1 to 3.5:1. General-  
10 purpose screws with a feed length of 4 – 8 D, compression length of 8 – 12 D, and a metering length of 6-10 D are acceptable for the extrusion of TPSiV materials. Screws with a pin or mixing section are recommended to provide a homogenous melt. The thermoplastic silicone rubber (TPSiV) is characterized as having excellent abrasion resistance, high temperature performance, bonds with various other polymers, and has  
15 low temperature flexibility and impact resistance.

The polymeric rubber used as the outer laminate of the tubing is derived from blends of polymeric materials comprising 10 to 30 and preferably 15 to 25 parts by weight of an olefinic polymer and particularly an ethylene-octene copolymer available from the Exxon Mobil Co. as EXACT 0201. Preferred olefinic polymers used in  
20 preparing these polymeric copolymers include ethylene copolymerized with suitable monomers such as C<sub>2</sub>-C<sub>8</sub> alpha olefins including propylene, butene-1, 1-pentene, 4-methyl pentene-1, hexene-1 and octene-1. The preferred comonomer is octene-1.

The second polymer of the polymeric blend comprises an ethylene, propylene, or styrene polymer or copolymer formed by a polymerization reaction in the presence of a catalyst preferably a metallocene. The preferred copolymer comprises 25 to 50 and preferably 35 to 40 parts by weight of a styrene-olefinic block copolymer available from the Dow Chemical Co as VECTOR 4111. More specifically, VECTOR 4111 is a linear, pure SIS triblock copolymer with narrow molecular weight distribution. The polymer is a low styrene, low modulus copolymer. It contained <1% diblock. It is the softest pure SIS triblock and has the highest elasticity. It has outstanding melt processability and is designed for use in elastomeric films or sheets and is a highly elastomeric compound.

VECTOR 4114 (diblock isoprene-styrene-isoprene-styrene) a highly elastomeric polymer can be substituted for VECTOR 4111. Further, a blend of VECTOR 4111 and 4114 will also provide an elastomeric compound. The properties of VECTOR 4111 are shown in Table I.

**TABLE I**

<b>Properties</b>	<b>Test Method</b>	<b>Unit</b>	<b>Typical Value</b>
<b><i>Resin Properties</i></b>			
Styrene	Dexco Method	Wt. %	18
Diblock Content	Dexco Method	Wt. %	<1.0
MFR <sup>(1)</sup>	ASTM D 1238	G/ 10 min	12
Ash	ASTM D 1416	Wt. %	0.3
<b><i>Physical Properties</i></b>			
Tensile Strength <sup>(2)</sup>	ASTM D 412	PSI	4000
300% Modulus <sup>(2)</sup>	ASTM D 412	PSI	275
Elongation <sup>(2)</sup>	ASTM D 412	%	1200
Hardness <sup>(3)</sup>	ASTM D 2250	Shore A	39
Specific Gravity	ASTM D 792	g/ee	0.93
<b><i>Product Form</i></b>			Dense Pellet

- (1) Condition (200°C/ 5 kg).
- (2) Typical values on compressions molded plaques, intended only as guides and should not be construed as specifications.
- (3) 1 sec. Dwell.

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The third polymer of the polymeric blend comprises 25 to 50 and preferably 35 to 40 parts by weight of a thermoplastic rubber available as VYRAM 9000 series. Vyram rubber is a thermoplastic vulcanizate (TPV) consisting of finely divided particles of partially crosslinked rubber in a continuous matrix of thermoplastic. Thus, it has the processability of a thermoplastic, but the properties and functional performance of a rubber. In polar fluids such as water and aqueous solutions, Vyram rubber retains its properties (with low volume swell) quite adequately and is comparable to Santoprene rubber. In non-polar fluids, especially at elevated temperature, the superiority of the latter becomes apparent.

15 In another embodiment, SANTOPRENE can be successfully employed in place of the VYRAM rubber. These materials are proprietary compositions commercially available from Advanced Elastomer Systems of St. Louis. The materials are characterized as thermoplastic rubber in which cross-linked rubber particles are dispersed throughout a continuous matrix of thermoplastic material with the rubber particles having an average size of 1  $\mu\text{m}$  and a hardness grade between about 55 Shore A and about 50 Shore D.

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In another embodiment, ethylene/vinyl acetate copolymers (EVA) can be used in place of the VYRAM rubbers. These polymers are selected from ethylene vinyl acetate

copolymers having a vinyl acetate percentage by weight relative to the ethylene in the range of 15-40 percent by weight. The term “ethylene-vinyl acetate copolymer” includes both the dipolymers and the terpolymers of ethylene with vinyl acetate and with carbon monoxide. Most commercial EVA dipolymers contain about 2-55 percent by weight of vinyl acetate. Terpolymers of ethylene with vinyl acetate and with carbon monoxide may contain about 18-40 percent by weight of vinyl acetate and 2-12 percent by weight of carbon monoxide. Polymers of ethylene with vinyl acetate are available from the E. I. Du Pont de Nemours and Company, under the trademark Elvax®. The terpolymers with carbon monoxide can be made according to the teachings of U.S. Patent No. 2,495,286.

The fourth polymer of the polymeric blend comprises about 2 to 15 and preferably 4 to 10 parts by weight of a maleic anhydride-olefinic copolymer available as EXXELOR-VA1803 from the Exxon Mobil Co. Exxelor VA 1803 is a high flow, amorphous ethylene copolymer functionalized with maleic anhydride by reactive extrusion. Its fully saturated backbone results in outstanding thermal and oxidative stability leading to enhanced weatherability. Moreover, its amorphous nature exhibits impact resistance at very low temperatures in blends with other polymers

**Properties of EXXELOR-VA 1803 are shown in Table II.**

TABLE II

Property	Exxon Mobile Test Method (based on)	Unit	Exxelor VA 1803
Maleic anhydride graft level	FTIR EPK-04 QT-02		High (*)
Melt flow rate (2.16 kg/230°C)	ASTM D 1238	g/10 min	3
Melt flow rate (10	ASTM D 1238	g/10 min	22

kg/230°C)			
Density	DIN 53479	g/cm <sup>3</sup>	0.66
Glass transition temperature (T <sub>g</sub> )	D8C	°C	-57
Volatiles	AM-S 350.03	%	0.15 max.
Color	ASTM E 313-96	Yellowness Index Pellet	25 max

(\*) MA level is typically in the range of 0.5 to 1.0 wt%

The values indicated in the table describe typical properties but do not constitute specification limits.

5           The fifth material of the polymeric blend comprises about 0 to 1.0 and preferably 0.4 to 0.6 parts by weight of phenolic resins obtained from Schenectady International Inc. as SP-1045. SP-1045 Resin is a heat reactive octylphenol-formaldehyde resin which contains methylol groups. It was specifically designed for the cure of isobutylene-Isoprene (Butyl) rubber by the resin cure system. The octyl group also makes SP-1045  
10 Resin compatible with elastomers, and can yield products offering a wide range of properties. In addition, the methylol groups can be used as functional sites for a variety of reactions.

Other phenolic resins useful in this invention include the novolac resins. Novolac resins are described in the Encyclopedia of Polymer Science and Engineering, Volume  
15 11, pages 45-95 (1985). Thermoplastic novolac resins are produced when a less than stoichiometric amount of formaldehyde is reacted with phenol in an acidic solution. In general, novolacs do not contain hydroxymethyl groups and will not crosslink simply by heating. Examples of the novolac resins useful include, but are not limited to, phenol-formaldehyde, resorcinol-formaldehyde, p-butyl phenol-formaldehyde, p-ethyl phenol-formaldehyde, hexyl phenol-formaldehyde, p-propyl phenol-formaldehyde, pentyl  
20 phenol-formaldehyde, p-octyl phenol-formaldehyde, p-heptyl phenol-formaldehyde, p-

nonyl phenol-formaldehyde, bisphenol-A-formaldehyde, hydroxynaphthalene formaldehyde and the alkyl (such as t-butyl) phenol modified esters of rosin. The various novolacs resins differ in their R substituted group, melting points, viscosities and other physical properties.

5           The flexible elastomeric tubing of this invention can be prepared by forming laminates of the thermoplastic silicone rubber (TPSiV), as the inner wall of the tube, with the polymeric rubber as the outer wall of the tube. The laminates can be made by coextrusion of these polymers and polymeric blends. The polymers are coextruded as layers directly in contact with one another, so that the resultant adhesion between layers  
10 occurs without a tie layer being needed, i.e., the coextrusion is carried out in the absence of any tie layer. When the coextruded laminate is in the form of tubing, the thickness of the layer can range from 6 to 18 mils e.g. with the conventional thickness being about 8 mils (0.2 mm).

          The following are specific examples illustrating the composition and method of  
15 preparing the flexible tubing of this invention.

#### EXAMPLE I

          Thermoplastic elastomeric TPSiV was extruded on a 50 mm (2.0 inch), 24:1 L/D, 2.5:1 compression ratio screw into a 0.1 mm thick (0.004") sheet. The TPSiV rubber was laminated onto the polymeric rubber derived from a polymeric blend comprising from  
20 about 20 parts by weight of an ethylene/octene copolymer, 35 parts by weight of a styrene-isoprene-styrene block copolymer, 35 parts by weight of a thermoplastic rubber (VYRAM 9201-45), 9.5 parts by weight of maleic anhydride-ethylene copolymer, and

0.5 parts by weight of a phenolic resin (SP 1045). The TPSiV and the polymeric blend were extruded on 50 mm (2.0 inch), 24:1 LD, 2.5:1 compression ratio extruder to form 4 mm (0.150 inch) thick sheet.

The conditions for the outer layer were as follows:

5	FEED ZONE 1	ZONE 2	ZONE 3
	140°C	160°C	170°C

	Adapter	Die
10	180°C	180°C

The conditions for the inner layer were as follows:

	FEED ZONE 1	ZONE 2	ZONE 3
15	170°C	180°C	190°C
	Adapter	Die	
	210°C	210°C	

#### EXAMPLE II (polymeric blend)

20 Parts by Weight

20	Ethylene/octene copolymer
35	Styrene-isoprene-styrene block copolymer
35	Ethylene/vinyl acetate copolymer
25 9.5	Maleic anhydride/ethylene copolymer
0.5	Phenolic resin

#### EXAMPLE III (polymeric blend)

30 Parts by Weight

20	Ethylene/octene copolymer
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40	Styrene/isoprene/styrene block copolymer
35	Thermoplastic Rubber (VYRAM 9201-45)
4.5	Maleic anhydride/ethylene copolymer
0.5	Phenol/aldehyde resin

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The peel strength of the TPSiV/polymeric rubber laminates was greater than 25 PLI (pounds per linear inch). The laminated flexible tubing of this invention is substantially resistant to bacterial growth and resistant to fat due to the inner laminate of the tube of silicon rubber (TPSiV). The outer layer or laminate of polymeric rubber is resistant to puncture and has good abrasion resistance. The flexible tubing of this invention is particularly useful as bacteria resistant tubing in milking systems and machinery. The aqueous systems include, but are not limited to water tanks, cooling waters and other water systems (e.g., intake cooling water, effluent cooling water, recirculating cooling water), and various other recirculating aqueous systems.

Further modifications of this invention will occur to persons skilled in the art and all such modifications are deemed to be within the scope of the invention as defined by the appended claims.